

**REUSE OF ALKALI CLEANING SOLUTIONS
AT STELCO INC.'S No 2 CONTINUOUS
ANNEALING LINE**

JANUARY 1996



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**REUSE OF ALKALI CLEANING SOLUTION
AT STELCO INC.'S No. 2 CONTINUOUS
ANNEALING LINE**

FINAL REPORT

Submitted to:

MINISTRY OF ENVIRONMENT AND ENERGY

**Under Terms of An Industrial Waste Diversion Program Agreement,
dated April 13, 1993**

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ABSTRACT

No. 1 and No. 2 Continuous Annealing Lines (No. 1 and No. 2 CA) at Stelco Inc.'s Hilton Works historically generated close to three million litres a year of spent alkali cleaning solution. To eliminate or reduce the need to dispose of this by-product, Stelco initiated a program to find a way to recycle the cleaning solution to the greatest extent possible.

Starting in March 1991, Stelco spent some two-and-a-half years developing a new system that makes possible continuous recycling of the solution. Featuring a state-of-the-art ultrafilter unit, the system removes residual oils and other contaminants from the solution in a way that had never been done before – on-line (sidestream) at a line operating temperature of ~82°C and at a pH of 12 to 13.

With financial assistance from the Ministry of Environment and Energy's (MOEE) Industrial Waste Diversion Program, Stelco installed a full-scale recycling system at No. 2 CA. Since October 1993, approximately 45 400 litres of alkali cleaning solution that previously had to be drained and disposed of *once a week* are now being recycled on a regular basis.

During the year (1994) that the alkali recycling system has been operational at No. 2 CA, solution changes (and disposal requirements) totaling 3.0 million litres have been avoided. By eliminating the need to dispose of this volume of solution, cost savings of approximately \$700 000 have been achieved.

With reduced alkali purchases added to energy and maintenance savings the total savings at No. 2 CA approached \$800 000.

Under the Industrial Waste Diversion Program Agreement with the MOEE, partial funding was to be provided for a similar recycling system at No. 1 CA. The recycling system was not installed at No. 1 CA, however, because the line was indefinitely shut down due to a reallocation of steel within Hilton Works.

This report, therefore, deals only with the development of the alkali cleaner recycling system and its application at No. 2 CA.

INTRODUCTION

The Cold Rolling and Coating Division of Stelco Inc.'s Hilton Works, in Hamilton, Ontario, operates a wide range of facilities which annually produces more than 1.2 million tonnes of cold rolled sheet, galvanized sheet and tinplate. Liquid by-products generated in association with this production level total nearly 12 million litres a year, virtually all of which historically was disposed of by a licensed hazardous waste handler.

More than five million litres of the liquid by-products (by far the largest individual component) are alkali cleaning solutions from six facilities that remove rolling oils and other contaminants from the steel strip prior to further processing. Two of these facilities, No. 1 and No. 2 Continuous Annealing Lines (No. 1 and No. 2 CA), account for some three million litres a year of the spent alkali cleaning solution.

The two lines, No. 1 CA with an annual steel strip throughput capacity of 100 000 tonnes and No. 2 CA with a capacity of 200 000 tonnes, are combined cleaning and annealing operations that prepare the strip for subsequent tinplate production.

Contaminants from the rolled strip render the cleaning solutions on these lines progressively less effective. The contamination is primarily in the form of residual and saponified oil, iron particulate and mill soils. Table I shows the composition of a typical contaminated (or spent) alkali cleaning solution.

Table II: Typical Chemical Makeup of Spent Alkali Cleaning Solution

Total Alkalinity (g/L)	Total Solids (caustic, iron, mill dirt) (%)	Iron (fines, soaps) (ppm)	Solid Load (free-floating oil, soaps) (%)
22.5	5.65	460	0.647

After the contamination level builds up to a point at which effective cleaning of the strip is inhibited, the various tanks must be drained and new solution made up, typically once a week in the case of the primary cleaning tanks on No. 1 and No. 2 CA. Disposing of the spent alkali cleaner from these lines was costing Stelco in the neighborhood of \$1 million annually.

Clearly, there was potential for significantly reduced environmental impact and for money to be saved if the frequency of disposing of these solutions could be reduced or, better still, if the need for disposal could be virtually eliminated.

In March 1991, Stelco began developing a technology for applying membrane ultrafiltration to extend the life of the cleaning solution. In membrane ultrafiltration, a semipermeable membrane is used to separate solid contaminant particles and large molecules (such as oils and salts of fatty acids) from the original solution.

A series of trials on a Hilton Works cleaning line with a small-capacity primary cleaning tank demonstrated that the embryonic alkali recycling system worked well. Given this successful result, plans were made to install commercial, full-scale systems on No. 1 and No. 2 CA.

An agreement was reached with the MOEE for financial support, under the Industrial Waste Diversion Program, for the purchase of an ultrafilter unit for each line. In October 1993, the alkali recycling system at No. 2 CA was successfully started up and brought into full-time service. This system has operated well from that time to the present (Appendix 1).

Plans to install the recycling system at No. 1 CA had to be changed because this line was indefinitely shut down due to changes in demand for tinplate.

This report, therefore, deals only with the development of the alkali cleaning solution recycling process and its application at No. 2 CA.

THE PROJECT

Developmental Approach

Various possibilities for resolving the alkali cleaner disposal problem were evaluated before it was decided to develop a state-of-the-art ultrafiltration system to remove the contaminants and permit the solution to be recycled.

The developmental goal was to treat the alkali solution continuously on-line (sidestream), at line temperature of ~82°C and at line pH of 12 to 13. Taking this approach would be *breaking new ground*, since previous work by other companies had centered around batch processing of the waste alkalis, off-line. Should the Stelco work be successful, a high level of recycling would be achieved, and the savings in treatment and disposal costs would be substantial.

Because of the novelty of this approach, Stelco organized a tripartite group to work on the development. The participants were Hyde Products, Inc., Cleveland, Ohio, the supplier of the ultrafilter units, Elf Atochem Canada Inc., Oakville, Ontario, a leading supplier of chemicals to the steel industry, and Stelco, in particular its Cold Mill Operating and Metallurgical personnel and selected R&D staff.

Developmental Trials

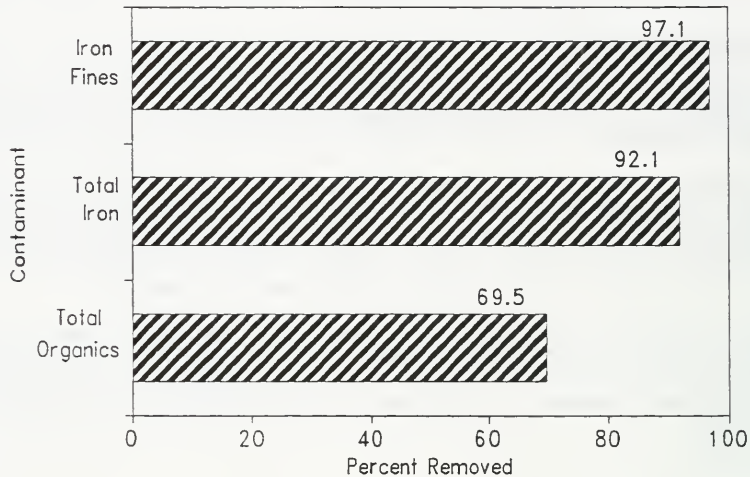
A series of seven developmental trials was conducted in late-1991/early 1992 on a cleaning line with a small-capacity, 4200-litre primary cleaning tank. The Hyde prototype ultrafilter unit used in these trials featured twin cylindrical cartridges, 7.5 cm in diameter by 64 cm in length, each containing hollow fiber membranes with a total filter area of 2.14 m². These higher pressure (~125 kPa) cartridges were later replaced, as part of the experimentation, with 102-cm-long lower pressure versions (~35 kPa). The lower pressure cartridges were designed for longer life, but reduced flux (Appendix 2).

The seven developmental trials showed that ultrafiltration technology can be used to successfully clean and recycle the alkali cleaning solution. From the first trial, which was a batch test on week-old alkali cleaner, to the final test, a five-week run to assess potential "long-term" operating problems, residual oil levels in the cleaning solution were reduced to less than eight parts per thousand (8 ppt) – and often approaching no measurable oil – within hours after the ultrafiltration system was connected.

Experience has shown that the performance of the cleaning solution progressively deteriorates as the residual oil level increases to, and moves above, 8 ppt. Therefore, the 8 ppt level is used as a guide to indicate if the solution has become contaminated to the extent that it should be drained and replaced.

Figure 1 illustrates a typical decrease in the residual oil (organics) content of the alkali solution – in this case about 70 percent – within a period of approximately 30 hours. Total iron and iron fines decreased by about 92 and 97 percent, respectively. Similar results were found in all trials if suitable operating conditions were maintained.

Figure 1: Contaminant Removal from Cleaning Solution after Processing for 30 hours through Ultrafiltration System



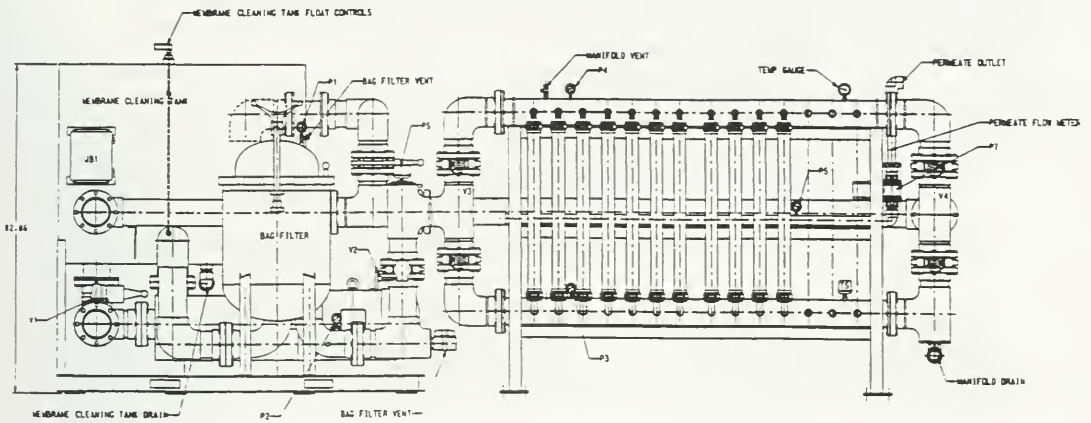
Since the outcome of the developmental trials was extremely positive, it was decided to proceed with the installation of a full-scale recycling system at No. 2 CA, applying the lessons learned in the trials to the design and operating procedures of the much larger capacity system. (No. 2 CA is the largest user of alkali cleaning solution at Hilton Works.)

Commercial System

With financial support from the MOEE's Industrial Waste Diversion Program for the purchase of a Hyde ultrafilter unit, a recycling system capable of processing the alkali cleaning solution in the 45 400-litre primary cleaning tank on No. 2 CA was commissioned in October 1993.

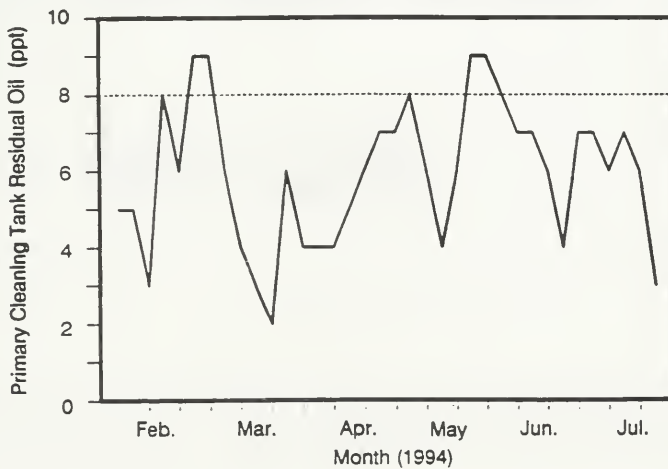
The system at No. 2 CA (see Figure 2) features 22 (expandable to 28) ultrafilter cartridges, each 7.5 cm in diameter by 102 cm long. Each cartridge contains hollow fiber membranes with a molecular weight cutoff rating of 30 K and having a total filter area of 2.04 m². A total average design flux of 34 litres per minute ensures that the entire volume of the cleaning solution in the primary cleaning tank can be turned over once every 24 hours.

Figure 2: Drawing of the Ultrafiltration System at No. 2 CA



Since the start of the commercial trials, residual oil contents in the alkali cleaning solution at No. 2 CA have almost continuously been less than the critical 8 ppt level. Figure 3 shows the cleaning solution oil levels for a six-month period ending in July 1994.

Figure 3: Residual Oil Levels in Alkali Cleaning Solution at No. 2 CA



The low residual oil readings have enabled the solution to be recycled continuously since the ultrafiltration system at No. 2 CA was started up. The few excursions above 8 ppt may have been caused by excessive soil on the strip and/or defouling irregularities, but the ultrafiltration system soon returned the oil content to an acceptable level.

Performance of the ultrafiltration system in full-scale commercial operation at No. 2 CA continues to be very good.

ENVIRONMENTAL AND ECONOMIC RESULTS

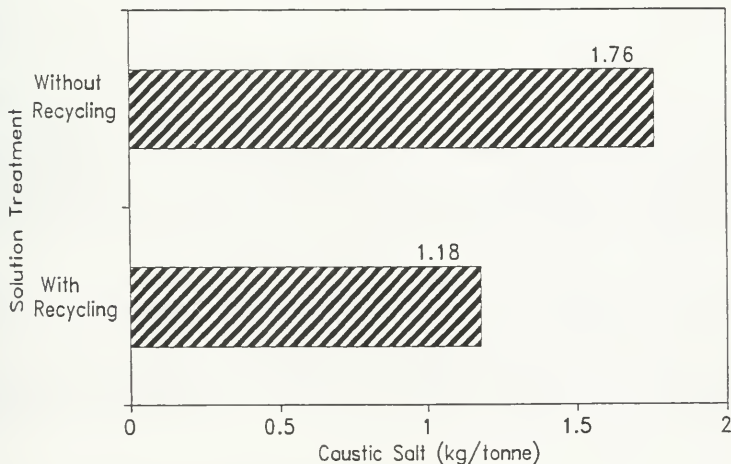
Decreased Waste Generation and Disposal Requirements

As noted in a previous section, since the start of commercial trials on No. 2 CA in October 1993, residual oil levels in the alkali cleaning solution have been held at less than 8 ppt, enabling the solutions to be continuously recycled and eliminating the need for disposal. During 1994, 52 solution changes of the primary cleaning tank totaling 3.0 million litres had been avoided.

Not having to dispose of these 3.0 million litres of liquid by-product from No. 2 CA represents a significant environmental contribution.

Figure 4, showing the amount of caustic salt consumed per tonne of steel processed with and without recycling, is additional evidence of improved performance made possible by recycling the alkali cleaning solution. The caustic salt consumption since the recycling system was commissioned in October 1993 is 33 percent less than it was in the months leading up to the start of recycling.

Figure 4: Caustic Salt Consumed per tonne of Steel Processed With and Without Recycling



Decreased caustic salt consumption means reduced demand for new production of sodium hydroxide and reduced quantities of this hazardous product which have to be transported on the Province's road and rail network. In addition, the decreased caustic salt consumption furthers Workplace Health and Safety objectives. Less on-site handling of the caustic is required and, as a result, worker exposure to the product is reduced.

The quality and consistency of the alkali cleaning solution also benefit from recycling. Continually "renewing" the solution ensures that its contaminant level remains low, thereby promoting consistent and thorough cleaning of the steel strip – a prerequisite to high quality products.

Cost Savings

Not having to dispose of 3.0 million litres of spent alkali cleaning solution from No. 2 CA represented a savings to Stelco of approximately \$700 000 for 1994.

With reduced alkali purchases, reduced energy consumption and maintenance costs, yearly savings made possible by recycling the alkali cleaning solutions at No. 2 CA approached \$800 000 (see Appendix 3 for a more detailed outline of the savings).

A more detailed summary of the advantages of the process are shown in Appendix 3.

IMPORTANT CRITERIA FOR ON-LINE RECYCLING OF ALKALI CLEANERS

During the developmental trials on the small-capacity cleaning line and, to date, during the running of the commercial ultrafiltration system at No. 2 CA, a number of physical and operational factors were identified as being important in the successful treatment of alkali cleaning solution. The factors include pre-filtration, solution temperature, membrane fouling and cleaning, membrane life, alkali composition, and material selection for fittings and valves. These factors are discussed briefly below.

Pre-Filtration

Good pre-filtration is necessary to maintain the integrity of the ultrafilter membranes. Two pre-filters were used in the developmental trials, one sized at 100 microns and the other at 25 microns. The composition of the filter bags proved to be important to the success of the trials. In some of the earlier runs, when polyethylene bags were used, holes the size of "loonies" were eroded in the bags because of the particulate matter, mainly iron, in the solution. After polypropylene bags were installed as replacements, no further pre-filtering problems were encountered.

Polypropylene pre-filters were incorporated into the ultrafilter design at No. 2 CA and have performed well since start-up.

Solution Temperature

Solution temperature was found to be a major factor affecting flux, i.e. the rate of flow of permeate through the ultrafilters. In one developmental trial, a 10°C increase to 60°C from 50°C doubled the flux – to about 6.1 litres per minute from 3.0 litres per minute. Similar findings were made in other trials, such that a relationship could be established, showing that each degree Celsius of solution temperature increase provides a flux increase of approximately 0.3 litres per minute.

Although there were many variables in the trials, it appears that for maximized flux, the higher the temperature the better, as long as it is below the safe upper operating limit of the membrane.

Processing solution from a bath operating at approximately 82°C exposes the ultrafilter membranes to temperatures close to the maximum desired. As noted in a previous section, at this high temperature, on-line processing of alkali cleaning solution is considered to be a world first.

Membrane Fouling and Cleaning

Membrane fouling is an important operating characteristic of ultrafiltration systems. If all other operating variables are held constant, fouling will cause the flux through the membrane to gradually decrease over time.

Fouling is caused by the deposition and accumulation of large molecules and/or particulate on the membrane surface, a buildup that progressively reduces the opportunity for solute to be filtered.

Many fouling problems during the trials at Stelco were, in large part, the result of downtime caused by hardware difficulties. The temperature drop that occurs when the operation is interrupted causing settling of material in the solution appears to affect the membrane and contribute to increased fouling.

To control fouling, Stelco and its project partners have modified the alkali cleaner and introduced a modified backflush and system-reversal practice. We have also determined what cleaning medium is most effective for our system and membranes.

Based on our experience and that of other membrane users, each situation requires some preliminary work to determine the optimum practice to mitigate the effects of fouling.

Membrane Life

One of the unknowns at the outset of the development work was the service life of the membranes. The partners, in conjunction with the membrane supplier, improved the membrane to the point that continuous operation for one year without replacement has been achieved, a record unheard of in the industry.

The latest version of the membrane incorporates a new "no macrovoid" concept, improved robustness in housings and fittings, and the most up-to-date component assembly (gluing) techniques.

Alkali Composition

The trial work demonstrated that the chemical composition of the alkali cleaner can affect the performance of the ultrafiltration system, particularly the resistance of the ultrafilter membranes to fouling. Care must be taken to identify and eliminate any constituent known or found to cause fouling, and to introduce substitutes that are compatible with both the ultrafiltration operation and the cleaning job required of the alkali solution.

Materials Selection for Alkali Recycling Systems

A number of hardware problems were encountered in the developmental trials. These problems emphasized the need for careful selection of materials and design of components to operate successfully at the temperatures, pressures and pH levels involved.

Some early difficulties with inconsistent pressure differentials across the membranes in the filter cartridges prompted an examination of the various valves and fittings. The trim of the ball valve regulating pressure across the membranes was found to be severely warped and stress-fractured. This and the other valves and fittings were made of polyvinyl chloride (PVC) plastic, a material with borderline properties at the temperatures (60 to 80°C) and pressures (up to 415 kPa) being run at times in the earlier trials.

Chlorinated-polyvinyl chloride (C-PVC), a plastic capable of higher level service, was considered to be better suited to the conditions being experienced. Accordingly, C-PVC replacement valves and fittings were selected and installed on the developmental unit, with subsequent satisfactory results.

Although the C-PVC performed better than the PVC, it was generally agreed that stainless steel is the material of choice for long-term, commercial applications of the technology. The most critical parts of the unit designed and installed at No. 2 CA, therefore, are made of stainless steel, while those not as severely heat- or pressure-stressed are made of C-PVC.

CONCLUSIONS

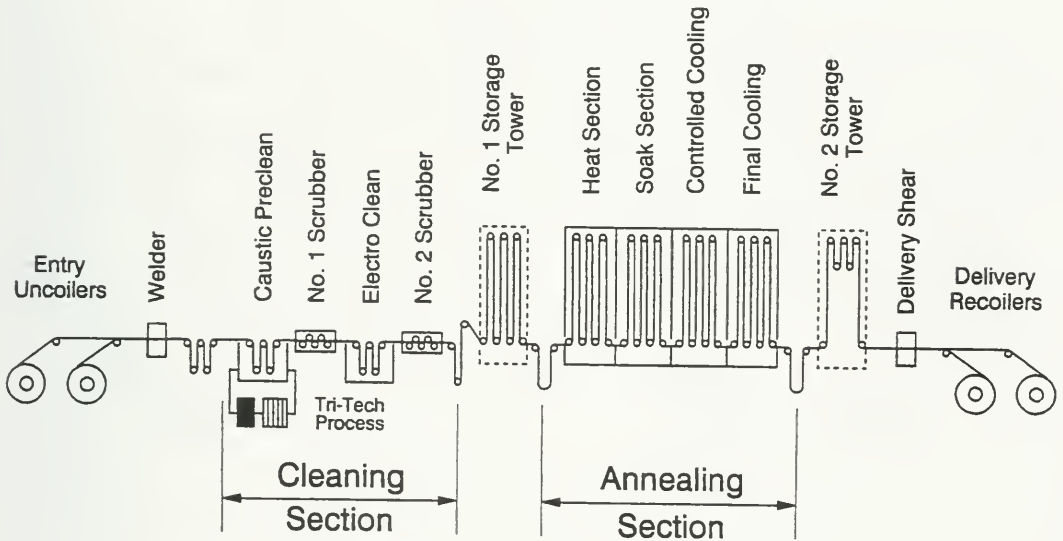
1. It is possible to recycle alkali waste cleaning solutions continuously, on-line, at operating temperatures of approximately 82°C and at a pH of 12 to 13.
2. Equipment that has been designed to recycle alkali cleaning solution is rugged enough to withstand the harsh environment and give reliable operating service.
3. No detrimental effects from prolonged recycling of the alkali solution were observed. The continuous solution makeup to compensate for evaporation and dragout may have helped prevent any untoward results.
4. Proprietary defouling techniques were developed to optimize the permeate flux.
5. Proper design of the pretreatment stage is important to the success of the technology.
6. Development of a recyclable alkali cleaner is important to the success of the technology.
7. New generation, macrovoid-free membranes with specially designed, robust housings have shown service life far in excess of that of traditional membranes.

RECOMMENDATIONS

1. This technology should be considered wherever waste alkali cleaning solutions are being disposed of by conventional methods, such as neutralization on-site, or waste hauling.
2. The process should continue to be improved with a goal of maximizing flux and, thereby, reducing operating and capital cost.

APPENDIX 1

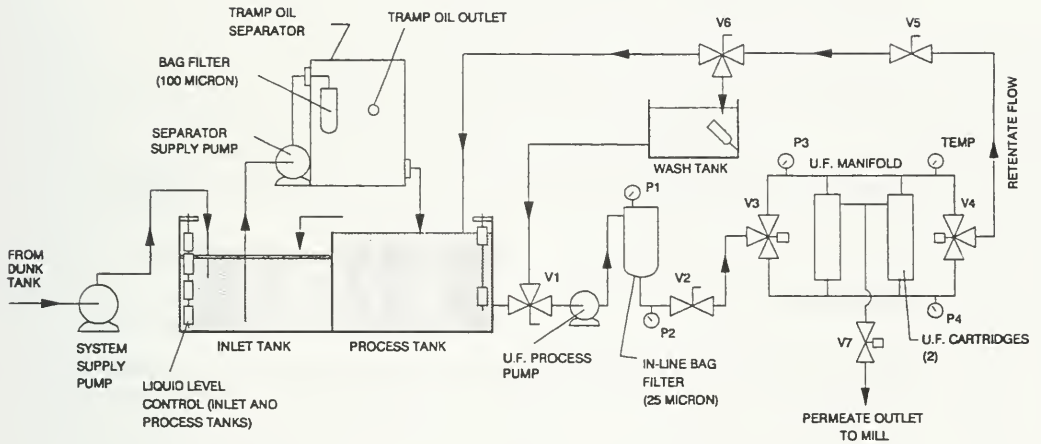
SCHEMATIC DIAGRAM OF No. 2 CA SHOWING THE LOCATION OF THE RECYCLING UNIT IN THE PROCESS STREAM



Stelco No. 2 CONTINUOUS ANNEALING LINE
Installed in 1962, this line continuously cleans and anneals light gauge strip primarily for tinplate orders.

APPENDIX 2

SCHEMATIC OF THE DEMONSTRATION UNIT USED TO PROVE THE TECHNOLOGY



APPENDIX 3

SUMMARY OF THE PROCESS ADVANTAGES AND ASSOCIATED COST SAVINGS

Stelco realized the following benefits in the first year of operation of the Tri-Tech Process:

- **Reduced Material Cost** – Purchases of chemical cleaners for the lines were reduced by 33 percent.
- **Decreased Cost of Disposal** – The cost to dispose of spent alkali was reduced by \$700 000.
- **Improved Strip Cleanness and Quality** – Rejuvenation and recycling enabled the solution to be maintained in "as-new" condition, thus ensuring optimal strip cleaning performance.
- **Reduced Environmental Liability** – Waste shipments decreased by 3.0 million litres.
- **Decreased Energy Requirements** – The cost of energy used to heat freshly made alkali baths was reduced by \$80 000.
- **Reduced Worker Industrial Hygiene Liability** – Handling of the waste solution by mill personnel was virtually eliminated.
- **Reduced Maintenance Costs** – Labor costs were reduced because tank cleanouts were no longer necessary.
- **Increased Line Availability** – The elimination of regular shutdowns for sludge removal increased line availability.

APPENDIX 4

A DETAILED DESCRIPTION OF THE DEVELOPMENT

Introduction

1. General Background

The Cold Rolling and Coating Division of Stelco Inc.'s Hilton Works, in Hamilton, Ontario, operates a wide range of facilities which annually produces more than 1.2 million tonnes of cold rolled sheet, galvanized sheet and tinplate. Liquid by-products generated in association with this production level total nearly 12 million litres a year, virtually all of which historically was disposed of by a licensed hazardous waste handler.

Almost half of the liquid by-products (by far the largest individual percentage) are alkali cleaning solutions from six facilities that remove rolling oils and other contaminants from the steel strip prior to further processing. These facilities are:

- Meaker Cleaning Line (annual capacity of 120 000 tonnes) – a continuous cleaning operation that prepares strip for batch annealing and subsequent cold rolled sheet or tinplate production.
- No. 1 Continuous Annealing Line (annual capacity of 100 000 tonnes) – a cleaning and annealing operation that prepares strip for subsequent tinplate production.
- No. 2 Continuous Annealing line (annual capacity of 200 000 tonnes) – a larger version of No. 1 Continuous Anneal (CA).
- No. 3 Electrolytic Tinning Line (annual capacity of 180 000 tonnes) – a continuous tinning operation with an integral alkali precleaning section.
- No. 1 Galvanizing Line (annual capacity of 120 000 tonnes) – a hot dip continuous galvanizing operation with an integral alkali precleaning section.
- The Z-Line (annual capacity of 315 000 tonnes) – a hot dip continuous annealing/galvanizing/galvannealing facility with an integral alkali precleaning section.

Contaminants from the rolled strip render the cleaning solutions on these lines progressively less effective. The contamination is primarily in the form of iron and sodium soaps from the fatty acids in the rolling oils, fatty acid carryover, iron fines, etc. Table I A4 shows the composition of a typical contaminated (or spent) alkali cleaning solution.

Table I A4: Typical Chemical Makeup of Spent Alkali Cleaning Solution

Total Alkalinity (g/L)	Total Solids (caustic, iron, mill dirt) (%)	Iron (fines, soaps) (ppm)	Soil Load (free-floating oil, soaps) (%)
22.5	5.65	460	0.647

After the contamination level builds up to a point at which effective cleaning of the strip is inhibited, the various tanks must be drained and new solution made up, as often as once per week in the case of the primary cleaning tanks on the Meaker Cleaning Line and No. 1 and No. 2 CA Lines. Disposing of the approximately 5 million litres of spent alkali cleaner was costing Stelco in excess of \$1 million annually.

Clearly, there was potential for reduced environmental impact and for money to be saved if the necessity of disposing of these solutions could be reduced.

In March 1991, Stelco's president challenged all company personnel to direct even more effort to finding solutions to disposal problems within the gates of the plant. Cold Mill personnel, who had been working for some time to decrease the cost of liquid waste disposal, welcomed and accepted this challenge.

Given the size of Stelco's operations and the large amounts of energy, supplies and materials of all types required, reducing, reusing or recycling within the plant represented not only good environmental stewardship but sound economics as well.

2. Trial Background

Hyde Products, Inc. (Hyde), Cleveland, Ohio, through its Canadian agent, Elf Atochem Canada Inc. (Atochem), Oakville, Ontario, suggested to Stelco that its state-of-the-art ultrafiltration system, with newly engineered filter membranes, could be used for recycling Stelco's alkali cleaning solutions (Stelco had experimented with an earlier generation ultrafiltration system in the past, with minimal success). Since Hyde was a pioneer in the development and use of ultrafiltration in industry, particularly in the separation of oily wastewater, it was decided to test the new system at Stelco.

Atochem also had a keen interest in the development in light of its primary function as a major supplier of chemicals to the steel industry. With Hyde, Atochem and Stelco each standing to benefit from a successful resolution of the alkali disposal problem, the three companies signed a tripartite agreement to share the costs of the trial work.

The developmental goal was to treat the alkali solution continuously on-line (sidestream), at line temperature of $\sim 82^{\circ}\text{C}$ and at line pH of 12 to 13. Taking this approach would be breaking new ground, since other companies had treated alkali wastes in batch processes, off-line. However, should the work be successful, savings in treatment costs, as well as disposal costs, would be substantial.

Ultrafiltration Theory

Before describing the successes achieved in the ultrafiltration trials at Stelco, it is useful to review some of the fundamental theory, principles and practices associated with membrane technology – the key to ultrafiltration and a number of other modern separation techniques.

1. The Nature of Membrane Filters

Although the first synthetic membrane was developed in 1865, it was not until 1907 that methods for controlling pore size were developed and the term ultrafiltration was coined. Ultrafiltration received a major boost in the late 1960s with the development of asymmetric noncellulosic ultrafiltration membranes. Asymmetric membranes feature a thin surface "skin" which prevents oversize particles or macromolecules from entering the main body of the membrane. Fouling

tendencies, therefore, are greatly reduced. Asymmetric membranes, made of polysulfone, were used in the alkali cleaner trials at Stelco.

Membranes are normally rated by numbers which refer to the molecular size or molecular weight above which a certain percentage of the solute in the feed solution will be retained under controlled conditions (e.g. temperature, pressure and flow rate). These ratings are called molecular weight cutoffs (MWCOs) and range from about 1000 to 1 000 000 (1 K to 1000 K). The MWCOs correspond to the approximate pore sizes shown in Table II A4.

Table II A4: Typical Relationship – Molecular Weight Cutoff and Pore Size of Asymmetric Membranes

MWCO	Approximate Pore Size (nm)
1 000	2
10 000	5
100 000	12
1 000 000	28

Asymmetric membranes are typically formed by dissolving a polymer in a suitable solvent, such as acetone, dioxane, pyridine, etc, depending on its acetyl content, and a swelling agent which may be magnesium perchlorate or formamide. When the solution is cast and the solvent allowed to evaporate, an increased concentration of polymer occurs at the evaporative surface. This forms the so-called "skin" layer, characteristic of asymmetric membranes.

The membranes are usually assembled into one of four types of module: hollow fiber (the type used in the Stelco trials), spiral wound, tubular and flat sheet.

2. Operation of Ultrafiltration Systems

Ultrafiltration technology uses the cross-flow principle, according to which the filter surface is constantly swept clean by the feed solution. The volumetric rate of flow parallel to the membrane surface is referred to as the flow rate of the fluid being treated.

The rate of flow of the permeate through the membrane, a major consideration in ultrafiltration, is referred to as "flux" and is usually expressed in terms of volume per unit of area per unit of time. The flux is directly proportional to the applied pressure and inversely proportional to the viscosity of the solution. Since viscosity is primarily controlled by two factors, solids concentration and temperature, increased temperature should increase the flux. Feed concentration, flow rate and turbulence in the feed channels also affect the flux through a membrane.

Because membrane flux is usually measured with pure water, any reading in service is an indicator of relative flux only. The actual flux will be influenced by:

- membrane properties
- feed solution properties
- concentration polarization
- membrane fouling

Fouling is the most important factor in the performance of membranes and is difficult to predict. In all, there seems to be no substitute for experimental trials to determine if a particular membrane material/module configuration is suitable for a particular application.

3. Characteristics of Polysulfone Membranes

Polysulfone membranes were used exclusively in the alkali cleaner recycling work at Stelco. These membranes are widely used in ultrafiltration applications, primarily because of the following characteristics:

- Wide temperature range: typically, can tolerate temperatures up to 82°C. Some manufacturers are claiming temperatures as high as 125°C.
- Wide pH tolerances: polysulfone can be continuously exposed to pHs from 1 to 13. This is a definite advantage for cleaning purposes because both acids and alkalis can be used to defoul the membrane.
- Fairly good chlorine resistance: typically up to 200 ppm chlorine can be used for short-term sanitation purposes, and up to 50 ppm chlorine for long-term storage of the membrane.
- Ease of fabrication: the membranes can be formed into a wide variety of configurations.
- Extended pore size range: a wide variety of pore sizes is available for ultrafilter applications, with MWCOs ranging from 1000 to 500 000 in commercial-sized modules.

The main limitations of polysulfone are the low pressure limits (~170 kPa with hollow fiber membranes of the type used in the Stelco work). However, this limit is well above the operating range of ultrafiltration units now in use at Stelco.

Demonstration Trials

1. Details

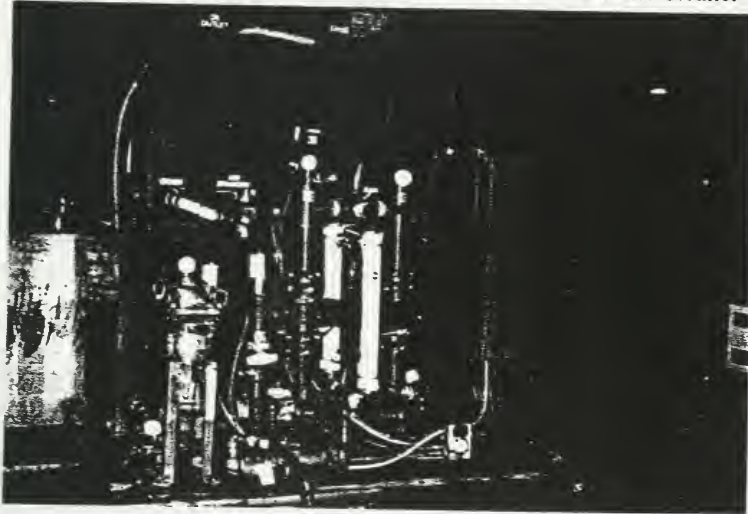
The initial, demonstration trials at Hilton Works were conducted on the 4200-litre entry-end primary cleaning tank of the Meaker Cleaning Line. This line was selected because it has a higher soil loading than the other lines and, hence, would provide a more severe test of the capabilities of the ultrafiltration technology.

In normal practice, fresh alkaline solution for the primary cleaning tank is made up each week. Specialized cleaners from Atochem and other suppliers, which can contain combinations of chemicals such as caustic soda, sodium silicate, surfactants, water softeners and defoamers, are mixed with water at a rate of 10 to 60 grams per litre. Over the course of a week, contaminant levels (of particular concern are rolling oils) gradually build up, rendering the solution progressively less effective in cleaning the steel strip passing through it. The solution is then drained from the tank and a new batch is made up.

Given this operating practice, it was clear that if the life of the cleaning solution could be extended by two, four, six weeks or more, substantial environmental and monetary savings could be realized.

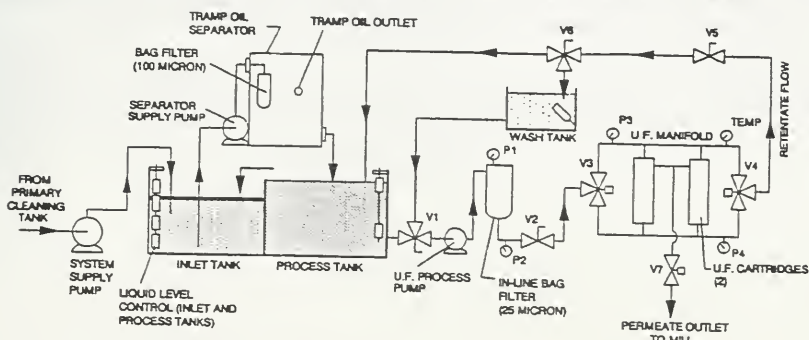
The prototype ultrafiltration unit supplied by Hyde for the demonstration trials featured twin cylindrical cartridges, 7.5 cm in diameter by 64 cm long, each containing hollow fiber membranes with a total filter area of 2.14 m². These higher pressure (~125 kPa) cartridges were later changed, as part of the experimentation, to 102 cm long lower pressure versions (~35 kPa). The lower pressure cartridges were designed for longer life, but reduced flux. Figure 1 A4 is a photo of the demonstration unit as installed for the trials.

Figure 1 A4: The Demonstration Ultrafiltration Unit at the Meaker Cleaner



The unit was capable of processing liquids through the ultrafilter at rates in excess of 3.8 litres per minute. This rate enabled the contents of the primary cleaning tank to be turned over every 24 hours. Figure 2 A4 shows how the unit was hooked up to the primary cleaning tank.

Figure 2 A4: Schematic of Component Hookup for Demonstration Trials



A newly developed polysulfone membrane material, which seemed particularly suited to the treatment of alkali cleaning solution because of its tolerance to high temperatures and high pHs, was selected for the trials. The membranes had MWCOs of either 100 K or 30 K.

A total of seven trials were run in late 1991 and early 1992, aimed at:

- establishing that ultrafiltration technology can be used in treating alkali cleaning solution at line temperatures ($\sim 82^{\circ}\text{C}$),
- determining if recycling can be done continuously (on-line) rather than by batch,
- demonstrating that permeate (cleaned alkali solution) quality is satisfactory (no significant stripping of certain useful components),
- confirming that steel surface cleanliness is equivalent to or better than that produced by current practice,
- demonstrating that the equipment will stand up to prolonged periods of use, and
- determining parameters and procedures for operating an ultrafiltration unit on a full-time basis.

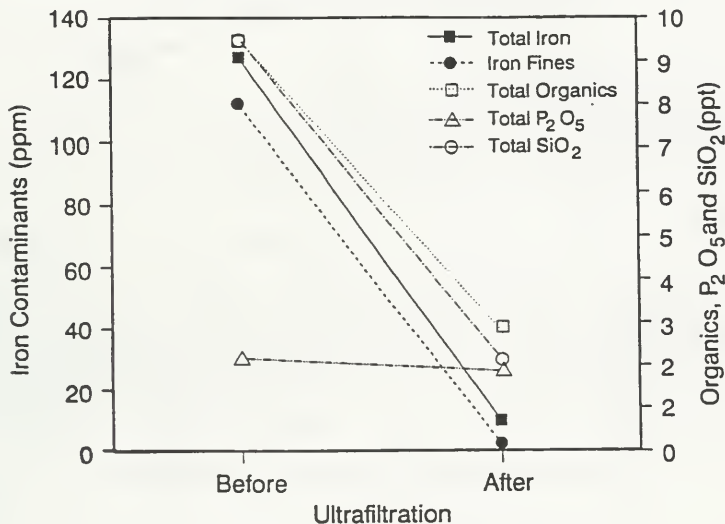
2. Results

(a) Solution Recyclability

The results of the seven demonstration trials showed that ultrafiltration technology can be used to successfully clean and recycle the alkali cleaning solution. From the first trial, which was a batch test on week-old alkali cleaner, to the final test, a five-week run to assess potential "long-term" operating problems, residual oil levels in the cleaning solution were driven below 8 parts per thousand (ppt) – and often approaching no measurable oil – within hours after the ultrafiltration unit was connected. The 8 ppt level is used as a guide to indicate if the solution has become contaminated to the extent that it should be drained and replaced.

Figure 3 A4 illustrates a typical decrease in the residual oil (organics) content of the alkali solution – in this case about 70 percent – within a period of approximately 30 hours. Total iron and iron fines decreased by more than 90 percent and phosphates, starting from a very low level, were reduced by about 10 percent. The silica content also decreased, a result that appears to be related to low-level silica deposition on the membrane and which was not a long-term effect. Similar results were found in all trials if suitable operating conditions were maintained.

Figure 3 A4: Solution Chemistry Before and After Ultrafiltration
– Demonstration Trial (30 K Membrane)



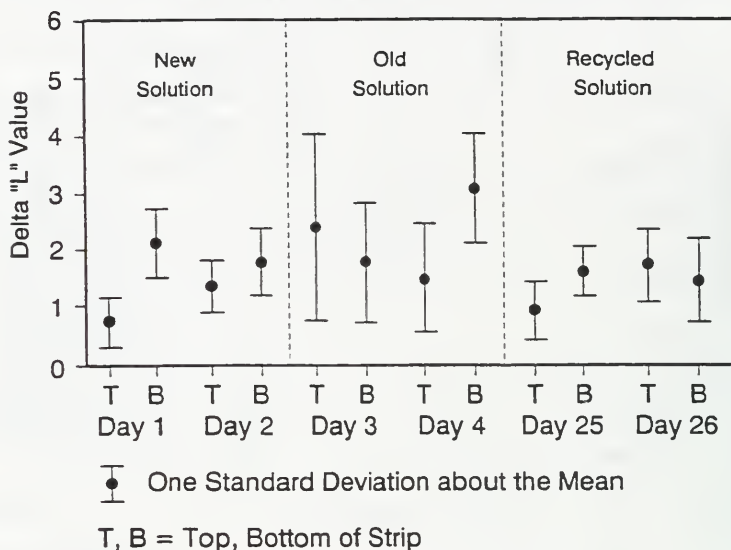
(b) Strip Surface Quality

Surface cleanliness was checked periodically during the trials using the tape test method. This method involves extracting surface impurities on high quality, clear cello tape strips, 55 mm x 100 mm, carefully placed on selected locations on the sample, and then comparing the extractions using a colorimeter. The relative difference in whiteness between the sample strips and a reference strip yields a number referred to as Delta "L", which is a measure of the degree of cleanliness.

Tape tests were performed during one demonstration trial in which 36 coils of the same steel type were cleaned in 12-coil lots in new (clean), old (dirty) and recycled cleaning solution. Analysis of the results showed that surfaces cleaned in the new or recycled solutions were equivalent, and better than surfaces cleaned in the old solution.

Figure 4 A4, taken from another trial, shows a comparison of the results of surface cleanliness analyses for coils cleaned in recycled solution and in nonrecycled solution during an earlier period. As in the 30-coil trial, surface cleanliness values for the samples processed through the recycled solution showed no statistically significant difference from the cleanliness values of the samples processed through the nonrecycled solution.

Figure 4 A4: Mean Surface Cleanness for Coils Cleaned in Demonstration Trials and in an Earlier Period



(c) Strip Coating Performance

As with surface cleanness, tinplating performance of the cleaned strip was checked during several trials. Stelco Metallurgical personnel recorded pinholes for each test coil and carried out hourly checks of total coating, iron-tin alloy and passivation performance. Visual inspection observations were also noted.

The results indicated that recycling of the alkali cleaning solution on the Meaker Cleaner had no negative effects on tinplating of the test coils. Pinhole, coating, alloy and passivation numbers were excellent. Visual inspections revealed no conditions, e.g. haze, that were considered to be serious and which could be associated with the trials.

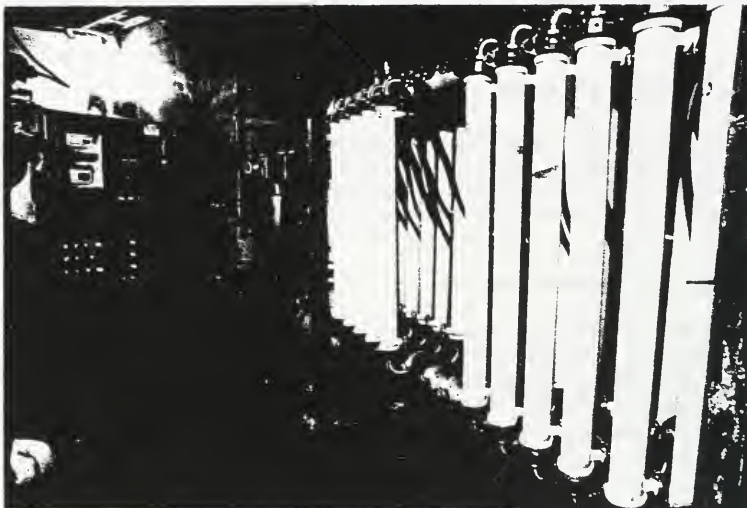
3. Practice and Design Optimization

Subsequent to the test work on the Meaker Cleaning Line, the demonstration ultrafiltration unit was tested for several weeks on each of No. 2 Continuous Annealing Line, (No. 2 CA), No. 1 CA and No. 3 Electrolytic Tinning Line. With these lines having primary alkali cleaner tank capacities of 45 400, 6400 and 9500 litres, respectively, the demonstration unit was clearly undersized at 3.8 litres per minute if the tank contents were to be turned over once per day.

Nevertheless, as with the trials on the Meaker Cleaner, excellent results were obtained, with residual oil and iron contaminant levels trending downward, particularly so during periods of reduced steel throughput (the demonstration ultrafiltration system ran continuously at maximum rate).

Since the results of all of the demonstration trials were extremely positive, it was decided to proceed with the installation of a full-scale ultrafiltration unit on No. 2 CA (the largest user of alkali

Figure 6 A4: The Ultrafiltration System as Installed at No. 2 CA



This flux ensures that the entire volume of the cleaning solution in the primary cleaning tank can be turned over once every 24 hours (the present cartridges are lower pressure (~35 kPa) for extended life, but they may be replaced by a higher pressure design for improved flux).

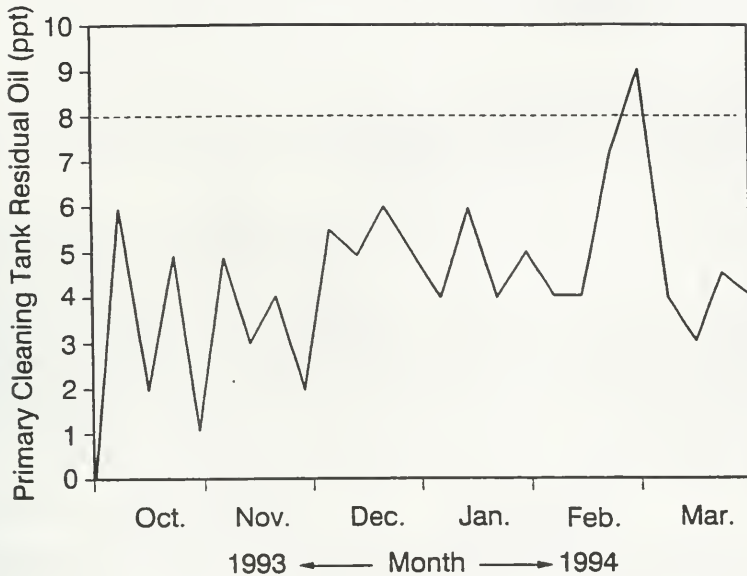
The system also includes a membrane cleaner tank for making up and holding solutions to flush, clean or descale fouled membranes, in situ. As an alternative to in situ cleaning, a separate 10-cartridge-capacity system has been provided for off-line cleaning of membranes. Off-line cleaning permits the ultrafiltration unit to be run for longer periods of time, with a better overall flux rate, because the system does not have to be taken out of service for several hours for in situ membrane cleaning.

The refurbished ultrafiltration unit reinstalled on a permanent basis at the Meaker Cleaning Line is basically as described in Section 3.1, but with more robust fittings, piping, etc where needed. Also, higher pressure (~125 kPa) ultrafilter cartridges with smaller diameter hollow fiber membranes were selected. These membranes have a filter area of 3.89 m², rather than the 2.14 m² of the membranes used previously. These higher capacity, higher flux ultrafilters are being evaluated for potential future application on the No. 2 CA unit.

2. Results and Trends

Since the start of the commercial trials, residual oil contents in the alkali cleaning solutions at both No. 2 CA and the Meaker Cleaner have consistently been less than 8 ppt, the level above which the solutions are considered spent and, therefore, requiring disposal. Typically, the 8 ppt level would have been reached after a week's operation, such that it was virtually "normal" practice to change the solutions on a weekly basis. Figure 7 A4 shows cleaning solution oil levels for a six-month period – October 1993 through March 1994 – for No. 2 CA.

Figure 7 A4: Residual Oil Levels In Alkali Cleaning Solution at No. 2 CA



As indicated in Figure 7 A4, the low residual oil readings have enabled the solutions to be recycled continuously since the ultrafiltration unit at No. 2 CA was started up. The one excursion above 8 ppt may have been caused by excessive soil on the strip, but the ultrafiltration system soon returned the oil level to a more desirable reading.

Figure 8 A4 compares residual oil levels in January 1994 and January 1993, periods with and without ultrafiltration on No. 2 CA. The improvement in 1994 is readily apparent, with no solution changes being required because of the effectiveness of the ultrafiltration system. Figure 9 A4, showing the amount of caustic salt consumed per tonne of steel processed, is another indication of the improved performance made possible by recycling the alkali cleaning solution. The caustic salt consumption in the 6 month period ending at the end of March 1994 was 32 percent less than it was in the same period a year previously, a significant saving.

Figure 8 A4: Residual Oil Level in Alkali Cleaning Solution, With and Without Recycling

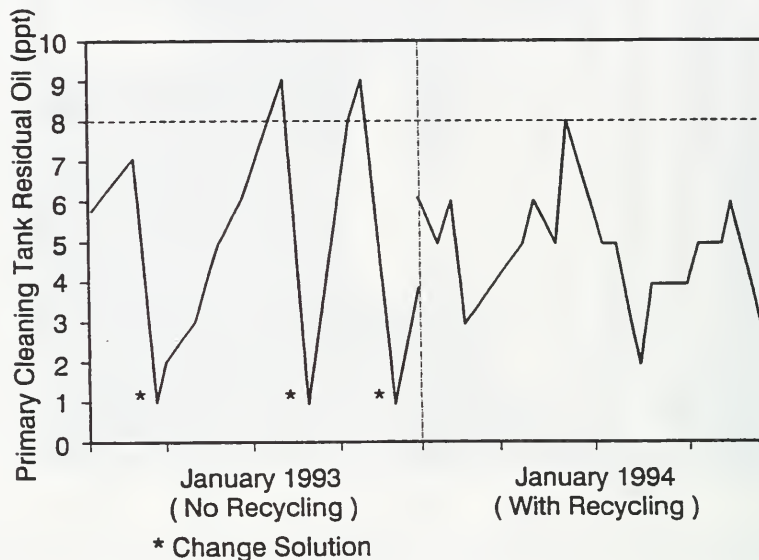
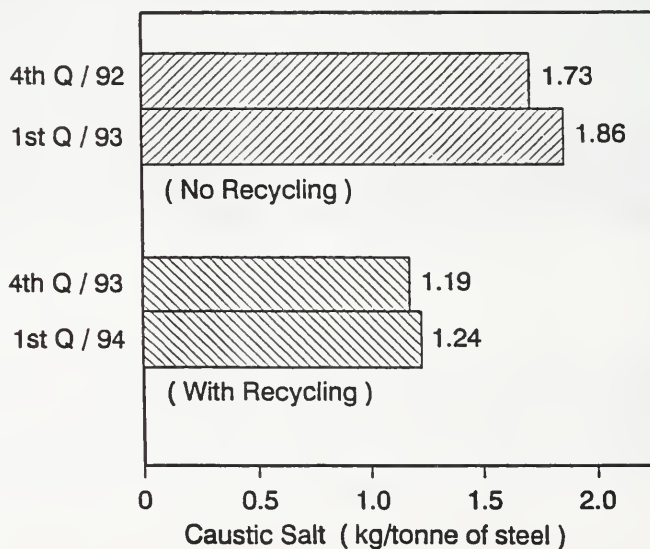


Figure 9 A4: Caustic Salt Consumed per tonne of Steel Processed, With and Without Recycling



During 1994, 52 solution changes totaling an estimated 3 000 000 litres from No. 2 CA and 52 changes totaling approximately 261 000 litres from the Meaker Cleaner had been avoided. Savings for this period were approximately \$800 000. Additional savings were realized from reduced alkali purchases.

The value of recycling alkali solutions through the use of ultrafiltration technology has clearly been proven at Stelco. Performance of the ultrafiltration systems in full-scale commercial operation continues to be very good. In anticipation of even better performance, an ongoing program is focused on optimization of flux, membrane pore size and other variables.

Important Factors in Ultrafiltration of Alkali Cleaning Solutions

During the trial work at the Meaker Cleaning Line and, to date, during the running of the commercial ultrafiltration systems at No. 2 CA and the Meaker Cleaner, a number of physical and operational factors were identified as being important in the successful treatment of alkali cleaning solution. The factors include pre-filtration, solution temperature, alkali composition, membrane fouling and cleaning, membrane pore size, and material selection for fittings and valves. These factors are discussed briefly below.

1. Pre-Filtration

Good pre-filtration is necessary to maintain the integrity of the ultrafiltration membranes. Two pre-filters were used in the Meaker Cleaner trials, one sized at 100 microns and the other at 25 microns (see Figure 3 A4). The composition of the filter bags proved to be important to the success of the trials. In some of the earlier runs, when polyethylene bags were used, holes the size of silver dollars were eroded in the bags because of the particulate matter, mainly iron, in the solution. After polypropylene bags were installed as replacements, no further pre-filtering problems were encountered.

Polypropylene pre-filters were incorporated into the ultrafilter design at No. 2 CA and have performed well since start-up.

2. Solution Temperature

Solution temperature was found to be a major factor in flux rates, i.e. the rate of flow of permeate through the ultrafilters. In one trial at the Meaker Cleaner in which temperature was under study, a 10°C increase to 60°C from 50°C doubled the flux rate – to about 6.1 litres per minute from 3.0 litres per minute. Similar findings were made in other trials, such that a relationship could be established, showing that in the range studied, each degree of solution temperature increase provides a flux rate increase of approximately 0.3 litres per minute.

Although there were many variables in the trials, it appears that for maximized flux rate, the higher the temperature the better, as long as it is below the safe upper operating limit of the membrane.

Processing solution from a bath operating at approximately 82°C exposes the ultrafilter membranes to temperatures close to the maximum desired. As noted in a previous section, this high temperature, on-line processing of alkali cleaning solution is considered to be a world first.

3. Membrane Fouling and Cleaning

Membrane fouling is generally considered to be caused by the deposition and accumulation of particles on the membrane surface and/or the crystallization and precipitation of smaller solutes on the surface and within the pores of the membrane itself.

Many fouling problems during the trials at Stelco were, in large part, the result of downtime caused by hardware failures. The temperature drop that occurs when the operation is interrupted and the settling of material in the solution both appear to affect the membrane and contribute to increased fouling.

Ultrafiltration membranes are typically cleaned with a water flush, detergent flush or mild acid flush, depending on the severity of the fouling and the nature of the particles or solute causing the fouling. Whatever the cleaning regime selected, the Stelco trials showed that clean backup membranes are a necessity for continuous operation. A separate, off-line membrane cleaning unit, similar to that installed at No. 2 CA, is desirable. Such an arrangement promotes a more consistent alkali cleaning solution and more consistent strip surface properties.

4. Membrane Pore Size

The alkali cleaning solution trials were conducted using membranes with molecular weight cutoff ratings of either 30 000 or 100 000 (30 K or 100 K).

Because of unpredictable fouling problems, the number of variables involved and difficulties experienced with the hardware on the demonstration ultrafiltration unit, pore size selection has yet to be optimized. However, good results are being obtained with the 30 K membranes, which provide a higher quality permeate (more oil removal) than do the 100 K membranes. On the other hand, under a given pressure, flux through the 30 K membranes tends to be somewhat lower than those associated with the 100 K membranes.

There also were indications that the 100 K membranes, with their larger pore size, stripped less silicate from the solution than did the 30 K membranes. Silicates are added to the cleaning bath to provide a barrier coating that reduces sticking of adjacent laps of a coil during batch annealing. Silicate stripping, however, was judged not to be a problem with either membrane.

5. Alkali Composition

The trial work demonstrated that the chemical composition of the alkali cleaner can affect the performance of the ultrafiltration system, particularly the resistance of the filter membranes to fouling. Care must be taken to identify and eliminate any constituent known or found to cause fouling, and to introduce substitutes that are compatible with both the ultrafiltration operation and the cleaning job required of the alkali solution.

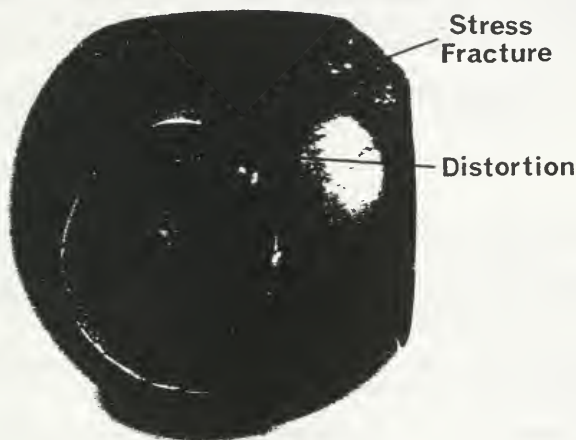
6. Materials Selection for Ultrafiltration Systems

A number of hardware failures were encountered in the early stages of the development work. These failures emphasized the need for careful selection of materials and design of components to operate successfully at the temperatures, pressures and pH levels involved.

Some difficulties with inconsistent pressure differentials across the membranes in the filter cartridges prompted an examination of the various valves and fittings. The trim of the ball valve

regulating pressure across the membranes was found to be severely warped and stress-fractured (see Figure 10 A4).

Figure 10 A4: Distortion and Failure of Trim In PVC Ball Valve



This and the other valves and fittings were made of polyvinyl chloride (PVC) plastic, a material with borderline properties at the temperatures (60 to 80°C) and pressures (up to 415 kPa) being run in the trials.

Chlorinated-polyvinyl chloride (C-PVC), a plastic capable of higher level service, was considered to be better suited to the conditions being experienced. Accordingly, C-PVC replacement valve and fittings were selected and installed on the demonstration unit, with subsequent satisfactory results.

Although the C-PVC performed better than the PVC, it was generally agreed that stainless steel is the material of choice for long-term, commercial applications of the technology. The most critical parts of the unit designed and installed at No. 2 CA, therefore, are made of stainless steel, while those not as severely heat or pressure-stressed are made of C-PVC.

Future Activities

The development and application of on-line, high temperature ultrafiltration of alkali cleaning solutions at Stelco is unquestionably an environmental and economic success story. Costs for disposing of spent cleaning solutions have been dramatically reduced, thereby generating an ongoing operating saving for Stelco. Similarly, environmental "disturbances" associated with neutralizing the caustic solutions and then landfilling the resultant salts have also been reduced. This success notwithstanding, research is continuing in order to further improve alkali recycling performance.

Because of the excellent results obtained to date, the three companies involved in the development – Atochem, Hyde and Stelco – agreed to make the technology available to the steel industry, worldwide. To this end, the companies have consolidated their efforts through a joint agreement and sought patent protection for the technology.

Hoping to build on the success of the alkali recycling development, Stelco is looking at expanding the use of the technology into other Cold Mill areas, e.g. to treat oily wastewater, detergents, etc. The objective is to establish, to the greatest extent possible, at-source separation and recycling. Success with this program will, in time, virtually eliminate the need for large-volume spent liquid disposal from the Cold Mill and further reduce Stelco's operating costs by several million dollars.

This is an ambitious objective, but one that, based on the accomplishments of the alkali recycling work, is considered to be achievable.

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